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Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 373 791
A1**

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EUROPEAN PATENT APPLICATION

21 Application number: 89312439.6

51 Int. Cl.⁵: H01M 4/50, C25B 1/00

22 Date of filing: 29.11.89

30 Priority: 07.12.88 JP 309396/88

43 Date of publication of application:
20.06.90 Bulletin 90/25

84 Designated Contracting States:
DE FR GB

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54 Lithium primary cell, cathode active material therefor and method for manufacturing manganese dioxide for cathode active material.

57 A lithium primary cell includes a cathode active material containing 0.05 to 2.0 parts by weight of phosphorus with respect to 100 parts by weight of manganese dioxide. A cathode active material for a lithium primary cell contains 0.05 to 2.0 parts by weight of phosphorus with respect to 100 parts by weight of manganese dioxide. A method for manufacturing electrolytic manganese dioxide comprises adding at least one member selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid and compounds thereof to an electrolyte upon manufacturing of electrolytic manganese dioxide by electrolysis using manganese sulfate and a sulfuric acid solution as the electrolyte.

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Lithium Primary Cell, Cathode Active Material Therefor, and Method for Manufacturing Manganese Dioxide for Cathode Active Material

BACKGROUND OF THE INVENTION:

Field of the Invention

The present invention relates to a lithium primary cell using lithium or a lithium alloy as an anode active material and manganese dioxide as a cathode active material, a cathode active material therefor, and a method for manufacturing manganese dioxide for the cathode active material.

Description of the Prior Art

Manganese dioxide and carbon fluoride are known as typical examples of a cathode active material of a lithium primary cell and are already commercially available.

Of these cathode active materials, manganese dioxide is advantageous since it has a good storage stability and is inexpensive.

A lithium primary cell using manganese dioxide as a cathode active material is currently applied to a camera and the like. As a multi-function of a camera has progressed, a demand has arisen for a lithium primary cell to have a high discharge voltage. A large discharge capacity, i.e., a long discharge time is also demanded for the lithium primary cell. No lithium primary cell, however, which can satisfy both the requirements with a good balance, has been proposed.

SUMMARY OF THE INVENTION:

The present invention has been made in consideration of the above situation and is intended to provide a lithium primary cell which uses manganese dioxide as a cathode active material and achieves both a high discharge voltage and a long discharge time, a cathode active material therefor, and a method for manufacturing manganese dioxide for the cathode active material.

The above object of the present invention is achieved by adding 0.05 to 2.0 parts by weight of phosphorus to 100 parts by weight of manganese dioxide and using the resultant material as a cathode active material of a lithium primary cell.

According to the present invention, manganese dioxide containing phosphorus is used as a cathode active material. When this cathode active material is used for manufacturing a lithium primary cell, both a high discharge voltage and a long discharge time are achieved.

It is case,d the content of phosphorus is generally 0.05 to 2.0 parts by weight with respect to 100 parts by weight of manganese dioxide. If the phosphorus content is less than 0.05 parts by weight with respect to 100 parts by weight of manganese dioxide, no sufficient addition effect is obtained in terms of discharge characteristics of a manufactured lithium primary cell. If the phosphorus content exceeds 2.0 parts by weight, discharge characteristics of manganese dioxide of a manufactured lithium primary cell are degraded.

Such manganese dioxide containing phosphorus is manufactured by, e.g., the following method.

That is, manganese dioxide containing phosphorus is manufactured by adding phosphoric acid, phosphorus acid, hypophosphorous acid, or a compound thereof to an electrolyte upon manufacturing of electrolytic manganese dioxide by electrolysis using manganous sulfate and a sulfuric acid solution as the electrolyte.

In this manufacturing method, manganese sulfate and a sulfuric acid solution are used as an electrolyte. Generally, in this electrolyte, a manganese concentration is 20 to 50 g/l, and a sulfuric acid concentration is 30 to 80 g/l. In addition, as electrodes, titanium or the like is used as a cathode, and carbon or the like is used as an anode.

Electrolytic conditions for electrolytic manganese dioxide are generally a bath temperature of 90 to 100 °C and a current density of 50 to 100 A/m².

In this manufacturing method, phosphoric acid, phosphorous acid, hypophosphorous acid, or a compound thereof is added to the electrolyte. Examples of the compound are a sodium salt, a potassium salt,

and the like of phosphoric acid, phosphorous acid, and hypophosphorous acid. The phosphoric acid compound or the like is uniformly added together with a manganese sulfate supply solution from an upper portion of an electrolytic cell to between electrode plates.

The concentration of the phosphoric acid compound or the like in the electrolyte is set to be 0.1 to 3.0 g/l, and the electrolytic conditions are adjusted so that phosphorus is contained in an amount falling within the above range in the manufactured electrolytic manganese dioxide.

The electrolytic manganese dioxide manufactured as described above has a large specific surface area of 40 to 150 m²/g. If the specific surface area of electrolytic manganese dioxide is smaller than the above value, reaction area with respect to an electrolyte is small and load discharge performance is weak when this electrolytic manganese dioxide is used as a cathode active material to manufacture a lithium primary cell. If the specific surface area of electrolytic manganese dioxide exceeds the above value, a cathode agent becomes bulky. The specific surface area of electrolytic manganese dioxide can be adjusted by arbitrarily selecting the type or content of the phosphoric acid compound.

A lithium primary cell, manufactured under normal conditions by using electrolytic manganese dioxide containing phosphorus as a cathode active material and lithium or a lithium alloy such as lithium-aluminum as an anode, has a higher discharge voltage and a longer discharge time than those of a conventional lithium primary cell.

BRIEF DESCRIPTION OF THE DRAWINGS:

Fig. 1 is a schematic sectional view for explaining a test cell used in examples and a comparative example; and

Figs. 2 and 3 are graphs each showing a relationship between a voltage and a continuous discharge time in the examples and comparative example.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT:

The present invention will be described in detail below by way of its examples.

Example 1

A titanium plate as a cathode and a graphite plate as an anode were alternately suspended in an electrolytic cell having a volume of 3 l and equipped with a heating apparatus, and an addition tube was connect to the bottom portion of the electrolytic cell to add an electrolytic supply solution composed of manganese sulfate and a phosphoric acid solution.

The electrolytic supply solution was adjusted so that 0.5 g/l of phosphoric acid were contained in the manganese sulfate solution.

When electrolysis was performed by supplying the supply solution in the electrolytic cell, the composition of the electrolyte was adjusted so that 50 g/l of manganese and 30 g/l of sulfuric acid were contained. Electrolysis was performed at a bath temperature of $95 \pm 1^\circ\text{C}$ and a current density of 100 A/m².

After electrolysis was finished, the cathode plate on which electrolytic manganese dioxide was electro-deposited was removed from the cell and subjected to a normal post-treatment, and the specific surface area of the obtained electrolytic manganese dioxide was measured. The measurement results are listed in Table 1.

A heat treatment was performed at 400°C for three hours, 0.135 g of the obtained electrolytic manganese dioxide were measured, and 0.09 g of graphite and 0.06 g of an tetrafluoroethylene resin were mixed therewith. The resultant mixture was pressure-molded at 3 t/cm² to prepare a cathode mixture. Note that the manganese dioxide, the graphite and the tetrafluoroethylene were predried and mixed.

The prepared cathode mixture was used to form a test cell as shown in Fig. 1, and a 2.5-K Ω continuous discharge test was performed at 20°C. All these operations were performed in a dry box in an argon atmosphere. The electrolyte was prepared by dissolving 1 mol/l of lithium perchlorate in a 1 : 1 solvent mixture of propylenecarbonate and 1,2-dimethoxyethane. A reagent used in this test was dried by a conventional method. In addition, the anode was formed by punching a metal lithium sheet to have the same diameter as that of the cathode mixture.

In the test cell shown in Fig. 1, reference numeral 1 denotes an anode terminal for externally extracting a current; and 2, insulating members made of a teflon resin. The insulating members 2 are threadably

engaged with each other to close the cell. Reference numeral 3 denotes an anode plate; 4, a crimped metal lithium sheet (anode); 5, a separator made of a non-woven fabric; 6, a cathode mixture formed by the above method; and 7, a stainless steel cathode.

A discharge test was performed by using the above test cell. The obtained relationship between a voltage and a continuous discharge time is shown in Fig. 2.

Examples 2 and 3

By using an apparatus similar to that used in Example 1, electrolysis was performed by changing a phosphorus addition amount as listed in Table 1, and a post-treatment was performed following the same procedures as in Example 1. The specific surfaces area of the obtained electrolytic manganese dioxides are listed in Table 1.

A heat treatment was performed following the same procedures as in Example 1, and a test cell as shown in Fig. 1 was manufactured following the same procedures as in Example 1 by using each electrolytic manganese dioxide. A discharge test was performed by using this test cell. The obtained relationship between a voltage and a continuous discharge time is shown in Fig. 2.

Examples 4 - 7

By using an apparatus similar to that used in Example 1, electrolysis was performed by adding phosphorous acid, hypophosphorous acid, sodium tripolyphosphate, and potassium tripolyphosphate in amounts as listed in Table 1, instead of phosphoric acid, and a post treatment was performed following the same procedures as in Example 1. The specific surfaces area of the obtained electrolytic manganese dioxides are listed in Table 1.

A heat treatment was performed following the same procedures as in Example 1, and a test cell was manufactured following the same procedures as in Example 1 by using each electrolytic manganese dioxide. A discharge test was performed by using this test cell. The obtained relationship between a voltage and a continuous discharge time is listed in Fig. 3.

Comparative Example 1

By using an apparatus similar to that used in Example 1, electrolysis was performed following the same procedures as in Example 1 except that no phosphoric acid solution was added, and a post-treatment was performed following the same procedures as in Example 1. The specific surface area of the obtained electrolytic manganese dioxide is listed in Table 1.

A heat treatment was performed following the same procedures as in Example 1, and a test cell as shown in Fig. 1 was manufactured following the same procedures as in Example 1 by using this electrolytic manganese dioxide. A discharge test was performed by using this test cell. The obtained relationship between a voltage and a continuous discharge time is shown in Figs. 2 and 3 so as to be compared with the examples.

Table 1

Example ° Comparative Example	Electrolytic Conditions						Electrolytic Voltage (V)	Specific Surface area (m ² /g)	Phosphorus Content of Electrolytic Manganese Dioxide *1
	Current Density (A/m ²)	Electrolyte Composition		Additive	Addition Amount (g/l)				
		Mn (g/l)	H ₂ SO ₄ (g/l)						
Example 1	100	50	30	H ₃ PO ₄	0.5	2.1 to 2.5	49	0.05	
Example 2	100	50	30	H ₃ PO ₄	1.0	2.1 to 2.3	63	0.52	
Example 3	100	50	30	H ₃ PO ₄	3.0	2.0 to 3.0	150	2.00	
Example 4	100	50	30	H ₃ PO ₃	0.5	1.8 to 2.1	56	0.63	
Example 5	100	50	30	Na ₅ P ₃ O ₁₀	1.0	1.6 to 2.0	60	1.53	
Example 6	100	50	30	K ₅ P ₃ O ₁₀	0.5	1.9 to 2.5	52	0.98	
Example 7	100	50	30	H ₃ PO ₂	0.5	1.8 to 2.1	60	0.68	
Comparative Example 1	100	50	30	-	-	1.9 to 2.3	38	0.0006	

*1 : amount (parts by weight) with respect to 100 parts by weight of manganese dioxide

*1 : amount (parts by weight) with respect to 100 parts by weight of manganese dioxide

As is apparent from Figs. 2 and 3, the test cell obtained by each of Examples 1 to 7 had a much longer continuous discharge time and a higher operation voltage during discharge than those of the test cell obtained by Comparative Example 1. That is, each test cell according to the present invention had very good cell characteristics as a non-hydrous electrolyte cell.

As has been described above, according to the method of the present invention, a phosphoric acid compound or the like is added in an electrolyte upon manufacturing of electrolyte manganese dioxide by electrolysis using manganese sulfate and a sulfuric acid solution as the electrolyte. Therefore, the obtained electrolyte manganese dioxide has a larger specific surface area than that of conventional electrolytic manganese dioxide and contains a predetermined amount of phosphorus.

In addition, by using this electrolytic manganese dioxide containing phosphorus as a cathode active material of a lithium primary material, a high discharge voltage and a long discharge time can be achieved.

Since the high discharge voltage and long discharge time can be simultaneously achieved, cell characteristics of the lithium primary cell can be effectively improved.

Claims

1. A lithium primary cell comprising a cathode active material containing 0.05 to 2.0 parts by weight of phosphorus with respect to 100 parts by weight of manganese dioxide.

2. A cathode active material for a lithium primary cell, containing 0.05 to 2.0 parts by weight of phosphorus with respect to 100 parts by weight of manganese dioxide.

3. A method for manufacturing electrolytic manganese dioxide, comprising:
adding at least one member selected from the group consisting of phosphoric acid, phosphorous acid, hypophosphorous acid and compounds thereof to an electrolyte upon manufacturing of electrolytic manganese dioxide by electrolysis using manganese sulfate and a sulfuric acid solution as the electrolyte.

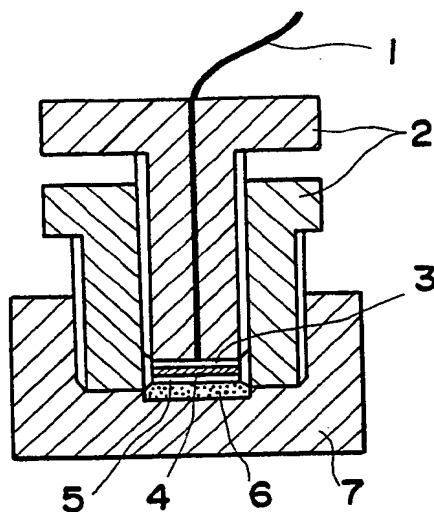


Fig. 1

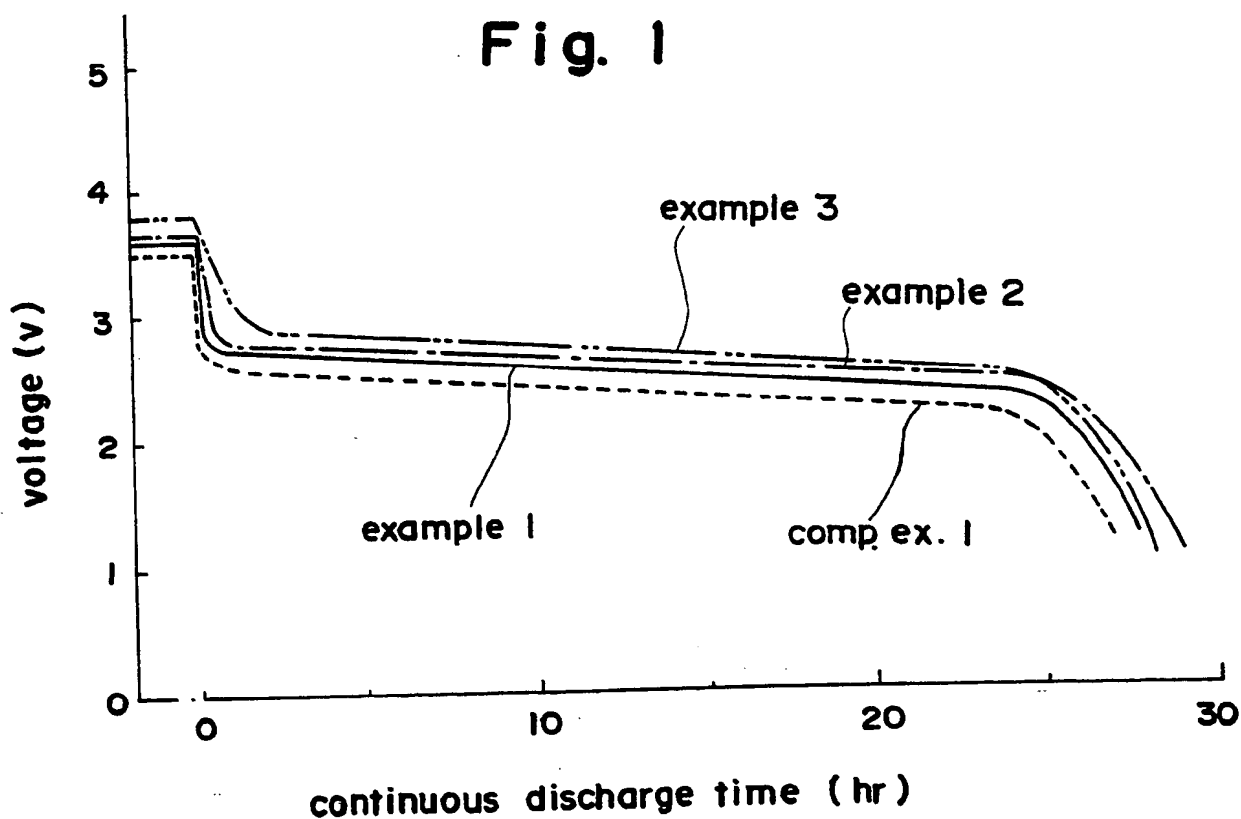


Fig. 2

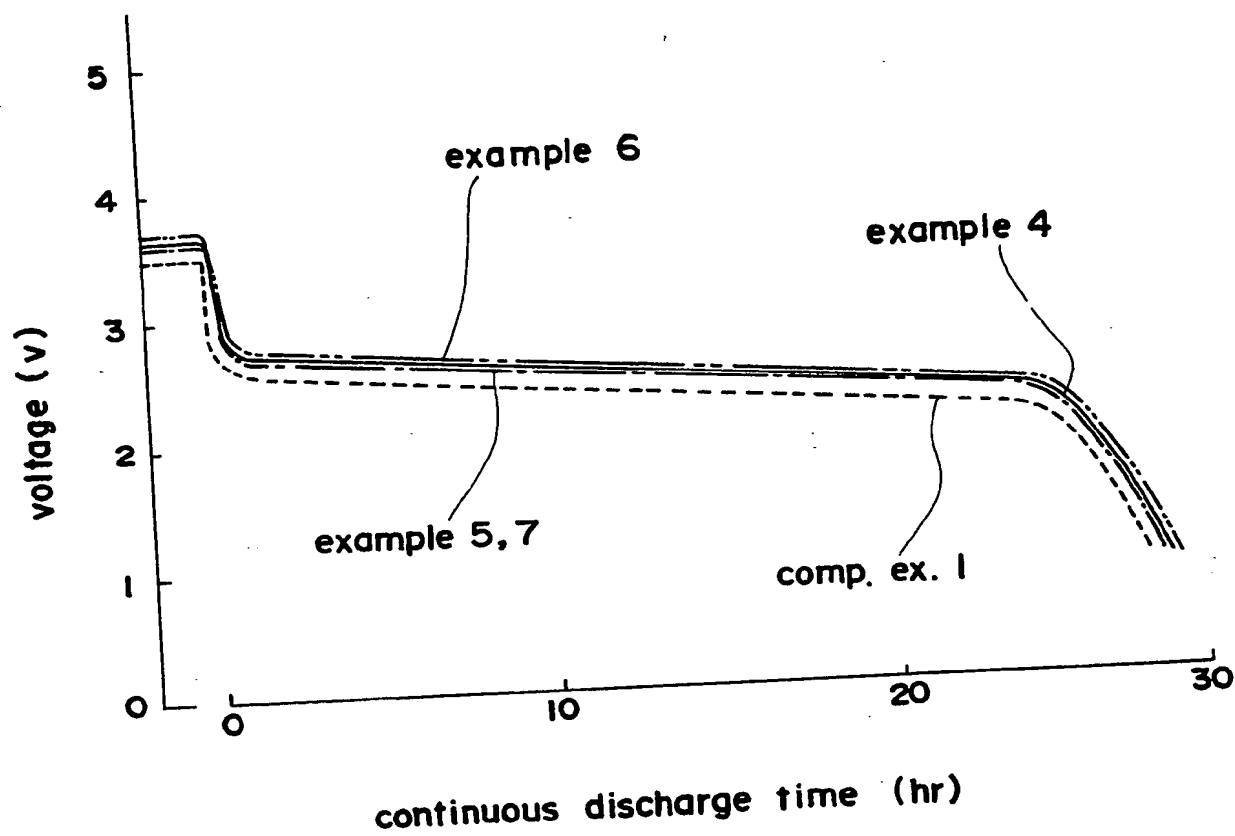


Fig. 3



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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2439

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 101, no. 20, 12th November 1984, page 540, abstract no. 179806w, Columbus, Ohio, US; F. GOLUBIOSCHI et al.: "Current efficiency and structure of electrodeposited manganese dioxide", & BUL. STIINT. TEH. INST. POLITEH. "TRAIAN VUIA" TIMISOARA, SER. CHIM. 1983, 28(1-2), 67-70 * Whole abstract *	3	H 01 M 4/50 C 25 B 1/00
X	CHEMICAL ABSTRACTS, vol. 95, no. 1, July 1981, page 535, abstract no. 15024w, Columbus, Ohio, US; I. TARI et al.: "Effect of the buffer capacity of electrolytes on the cathodic polarization of manganese dioxide electrodes", & DENKI KAGAKU OYOBI KOGYO BUTSURI KAGAKU 1981, 49(2), 91-5	3	
A	US-A-4 465 747 (W.P. EVANS) * Claims 1,2,10 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 478 921 (R.A. LANGAN) * Claims 1,4,6 *	1	H 01 M C 25 B
A	PATENT ABSTRACTS OF JAPAN, vol. 6, no. 128 (E-118)[1006], 14th July 1982; & JP-A-57 55 065 (SANYO DENKI K.K.) 01-04-1982 * Whole abstract *	1,3	
A	CHEMICAL ABSTRACTS, vol. 77, no. 20, 13th November 1972, page 560, abstract no. 134401e, Columbus, Ohio, US; & JP-A-72 02 419 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 22-01-1972		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-03-1990	Examiner D'HONDT J.W.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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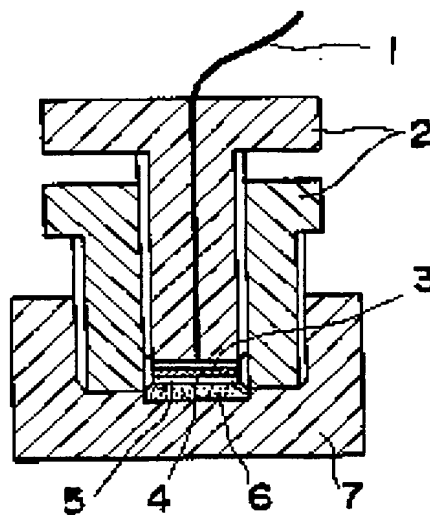


Fig. 1

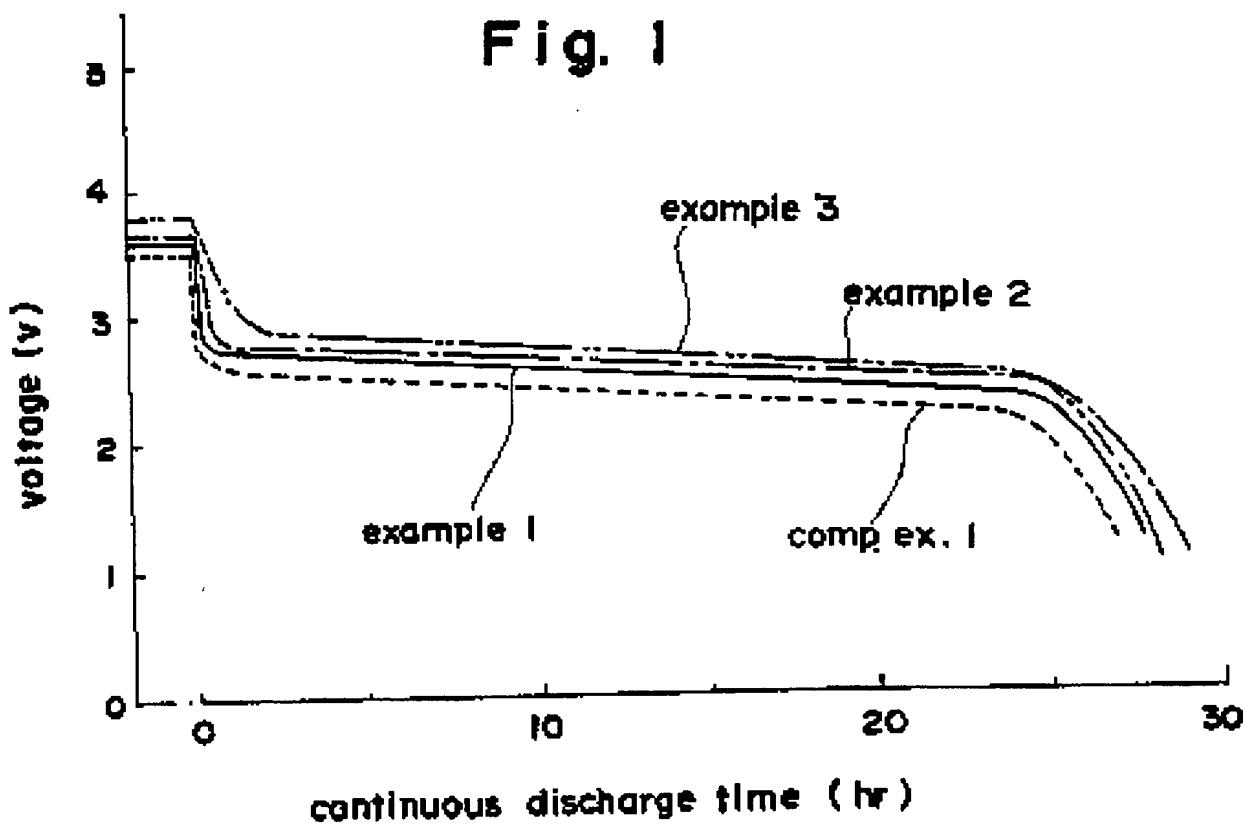
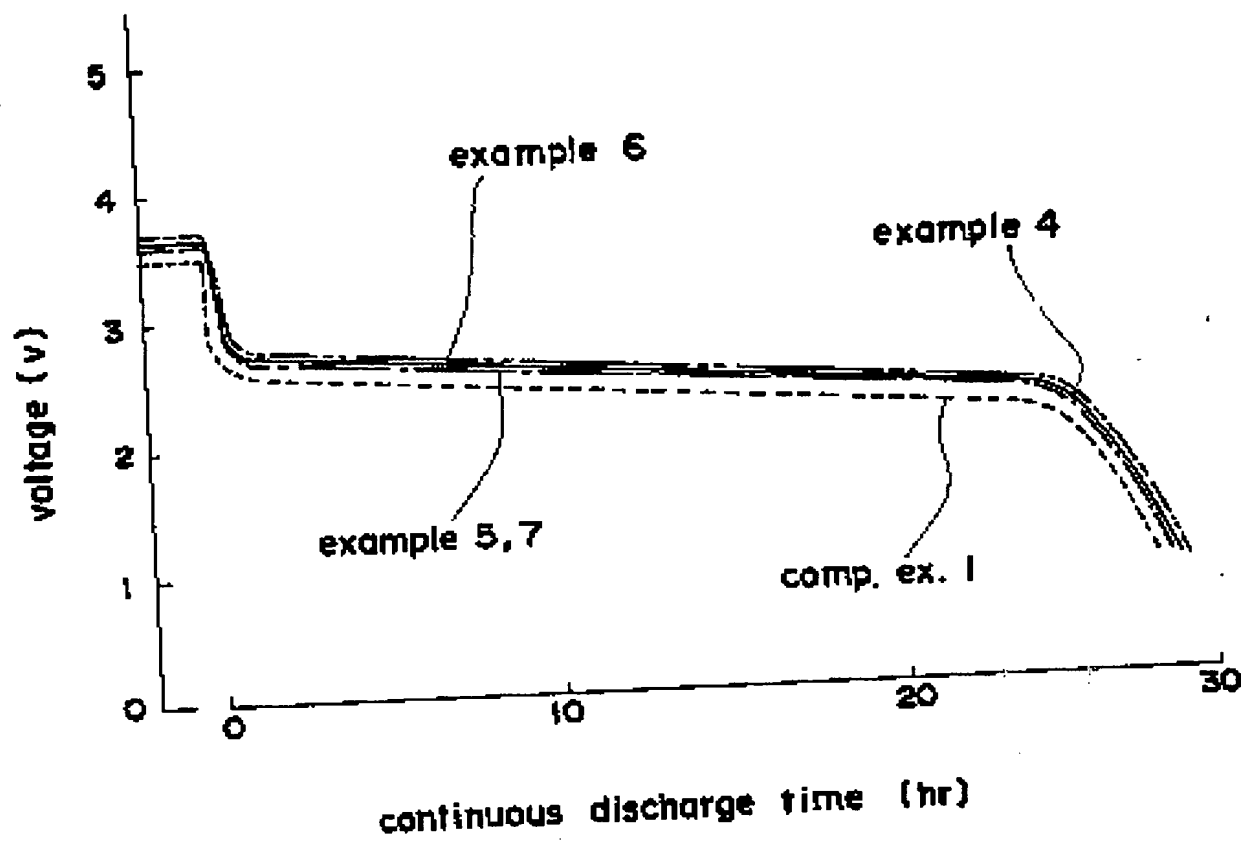


Fig. 2

**Fig. 3**